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GAS SCRUBBER, by JS McCall

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ANALYTICAL SUPPORT FOR ORGDP* PURGE GAS SCRUBBER

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ABSTRACT

At the Oak Ridge Gaseous Diffusion Plant large quantities of highly corrosive and toxic gases from the purge cascade are removed by means of an alkaline spray chamber. Analytical support of the operation of the scrubber unit is provided for reasons of process control, safety, uranium accountability, and environmental pollution concern. Analytical procedures and concentration ranges are presented for the liquids, gases, and solids encountered in the system.

This paper was prepared for oral presentation at the Second Annual UCC-ND Waste Management Seminar to be held at K-25 in March, 1979.

February 1, 1979

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*This document is based on work performed at the Oak Ridge Gaseous Diffusion Plant operated by Union Carbide Corporation Nuclear Division for the U. S. Department of Energy.

ANALYTICAL SUPPORT FOR ORGDP PURGE GAS SCRUBBER

The Oak Ridge Gaseous Diffusion Plant (ORGDP) operates an alkaline scrubber to remove toxic gases emitted from the diffusion process for uranium enrichment.

Routine operation of the scrubber presents analytical needs in three major areas of concern. Process control is important both to guarantee effective scrubbing and to maintain conditions which will minimize corrosion within the scrubber system. By-product disposal requires analyses for nuclear and chemical safety, uranium accountability, and environmental monitoring. The purge gas is monitored for environmental levels of toxic materials emitted to the atmosphere.

A simplified flow diagram of the scrubber is shown in Figure 1. The gas

PURGE CASCADE SCRUBBER SYSTEM

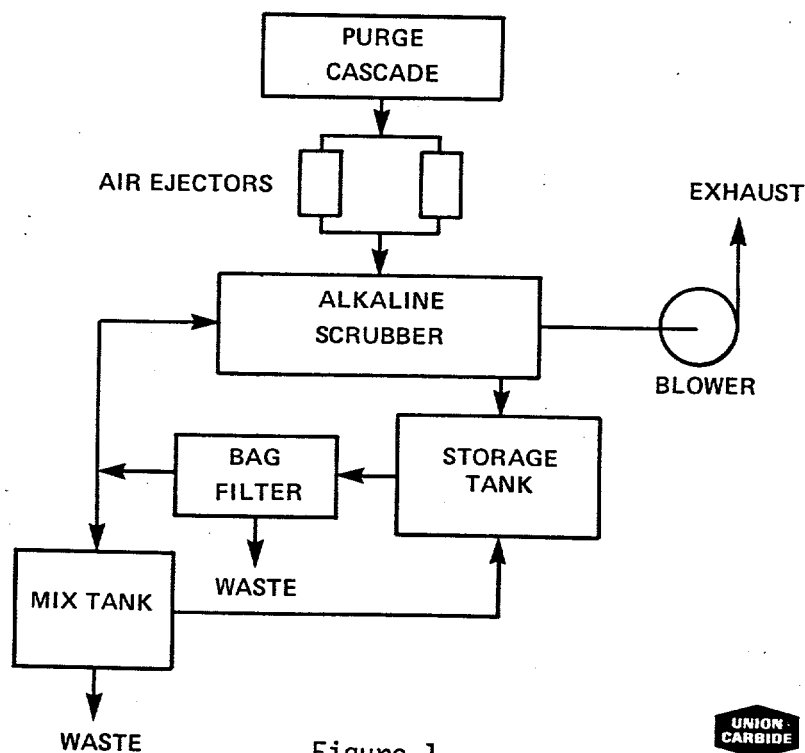


Figure 1

stream containing fluorine, uranium hexafluoride, chlorine trifluoride, technetium oxyfluoride and their reaction products is mixed with air from air ejectors and passes through the scrubber where contact with a spray of potassium hydroxide (KOH) solution removes the toxic gases. The KOH solution, which has absorbed the toxic compounds and also a large quantity

of carbon dioxide introduced by the air ejectors, is circulated into the storage tank where the bulk of the liquid is contained. The solution is continuously circulated from the storage tank through appropriate bag filters to remove undissolved solids, and thence back to the scrubber for additional contact. Solids are periodically removed from the bag filters and transferred to waste containers. In order to maintain high alkalinity and to reduce the dissolved solids content, the system is periodically "blown down". This is done by removing part of the used KOH solution and replacing it with fresh solution. That portion which is removed is transferred to the mix tank where it is analyzed before disposal. Provision is also made for regeneration of the recirculating solution by the addition of lime slurry to form insoluble calcium fluoride and KOH. This regeneration method was used initially, but has been replaced by a more extensive use of the "blowdown" operation.

Analytical support of the purge cascade scrubber is important to assure that the scrubber removes the toxic materials from the purge gas. Samples of the recirculating solution are analyzed for process control. Periodic chemical analysis of the recirculating solution is needed to maintain effective scrubbing and to control corrosion rates, thereby minimizing downtime. By-products are analyzed for nuclear safety, uranium accountability, and environmental waste management. The exhaust gas is analyzed for environmental levels of fluorine, chlorine, uranium, and technetium. Inlet gas samples have been analyzed to determine scrubber efficiency.

The parameters determined on the recirculating solution are divided into two groups, primary and secondary, based on their impact on the day-to-day control of the scrubbing process. Samples requiring analysis for the primary parameters are taken daily, and the analyses must be completed the same day. Samples requiring secondary parameters may be set aside for subsequent analysis.

The analytical methods used to determine the primary parameters and their ranges are described in Table 1. A pH measurement provides a quick check

Table 1

ANALYTICAL METHODS FOR RECIRCULATING SOLUTION

Primary Parameters	Method	Range
pH	Combination Electrode	10-14 ⁺
Alkalinity	Titrimetric	KOH 3-60 mg/ml K ₂ CO ₃ 25-90 mg/ml
Fluoride	Selective Ion Electrode	8-30 mg/ml
Density	Gravimetric	1.05-1.2 g/ml

on the alkalinity of the solution. It is measured using a combination electrode. Effective scrubbing requires the close control of the system's total alkalinity which is comprised of hydroxide ions and carbonate ions. The concentration of each ion must be determined. This is done by titrating to separate potentiometric end points. Occasionally the scrubbing solution becomes sufficiently acidic for potassium bicarbonate to be formed. When this happens, the bicarbonate concentration is also determined by the same procedure. Fluoride is monitored to control its concentration in order to minimize the corrosiveness of the solution. The fluoride concentration of the sample, after a hundred-fold dilution, is determined by a selective ion electrode (SIE) method. Density measurements are useful for indicating solution flow properties and total solids content and are made by weighing a 10-ml aliquot of the sample.

Table 2 shows the analytical methods and concentration ranges for the secondary parameters. The analysis of the solution for these ions, while not necessary for daily process control, is needed to monitor increases in their concentration so that their solubility limits are not exceeded.

Table 2

ANALYTICAL METHODS FOR RECIRCULATING SOLUTION

Secondary Parameters	Method	Range
U	TBP Extraction-Colorimetric	10-150 $\mu\text{g/ml}$
Cl	Selective Ion Electrode	5-35 mg/ml
ClO_3	Extraction-Colorimetric	2.5-15 mg/ml
ClO_4	Selective Ion Electrode	15-1000 $\mu\text{g/ml}$
Tc	Radiochemistry	0.01-0.6 $\mu\text{g/ml}$

The uranium is measured colorimetrically after extraction by a solution of tributyl phosphate (TBP) in Varsol. Chloride was originally determined titrimetrically. An SIE method has been evaluated for the chloride determination and is the method now in use. Chlorate is analyzed by an iodine release-colorimetric procedure. Perchlorate is determined directly by a selective ion electrode. Technetium is determined by radiochemistry. Chlorates and perchlorates are no longer run routinely since experience has shown that concentrations are not high enough to constitute a problem.

Waste by-products from the scrubber system consist of bag filter solids and blowdown liquid. Information gained from the analysis of the bag filter solids is used to fulfill the plant requirements for nuclear safety, to implement chemical safety practices, and for purposes of uranium accountability. Analyses of blowdown liquid samples are essential to compliance with plant nuclear safety requirements, for computing data for

uranium accountability, and for environmental waste management. Since the blowdown liquid is transferred to a holding pond, it is necessary to determine the levels of fluoride, chloride, uranium, and technetium introduced to the environment. Duplicate grab samples are taken from both waste by-products. The blowdown liquid samples are taken from the mix tank while the pumps are still running to provide mixing. Analytical methods for monitoring the two waste by-products from the recirculating system are presented in Table 3. Samples of the bag filter solids are analyzed colorimetrically for uranium that has been extracted into TBP.

Table 3
ANALYTICAL METHODS FOR RECIRCULATING
SYSTEM BY-PRODUCTS

Component	Method	Range
<u>Bag Filter Solids</u>		
U	TBP Extraction-Colorimetric	1-20 mg/g
ClO ₃	Extraction-Colorimetric	1-35 mg/g
ClO ₄	Selective Ion Electrode	0.1-1 mg/g
<u>Blowdown Liquid</u>		
U	TBP Extraction-Colorimetric	20-8000 µg/ml
Tc	Radiochemistry	0.01-0.07 µg/ml
F	Selective Ion Electrode	5-45 mg/ml
Cl	Selective Ion Electrode	1-10 mg/ml

Chlorate and perchlorate are determined in the bag filter solids after extraction into an aqueous medium. Aliquots of the extract are analyzed for chlorate and perchlorate by the methods already discussed. Chlorate is determined by the iodine release-colorimetric method and perchlorate is determined by the SIE method. In the blowdown liquid, uranium is analyzed by the TBP extraction-colorimetric method used for the recirculating solution. Technetium is analyzed radiochemically by the beta liquid scintillation method. For the blowdown liquid, fluoride and chloride are analyzed by the methods described for the recirculating solution. Chlorates and perchlorates are no longer run routinely after experience has shown that no problem is expected with the levels that are present.

To assure that the scrubber is performing its function in removing the toxic materials as the liquid and solid by-products, it is important to

analyze the purge gas. The sampling and analysis of the inlet and outlet gas is important for different reasons. The inlet gas is analyzed to determine the total amount of toxic material entering the scrubber. The efficiency of the scrubber is determined by comparing the inlet and outlet gases. The outlet gas is monitored for environmental levels of fluoride, chloride, uranium, and technetium. Routine inlet gas sampling was discontinued after enough data were collected for a good characterization of scrubber operation.

The sampling train used for gas sampling is shown in Figure 2. The gas is pulled through a series of two Boyce-Thompson collectors containing a KOH solution, to which glass beads have been added. The beads raise the contact surface area of the gas sample with the liquid, thereby increasing sampling efficiency. Sampling is conducted for 24-hr periods at flow rates chosen for an isokinetic velocity through the sampling probe.

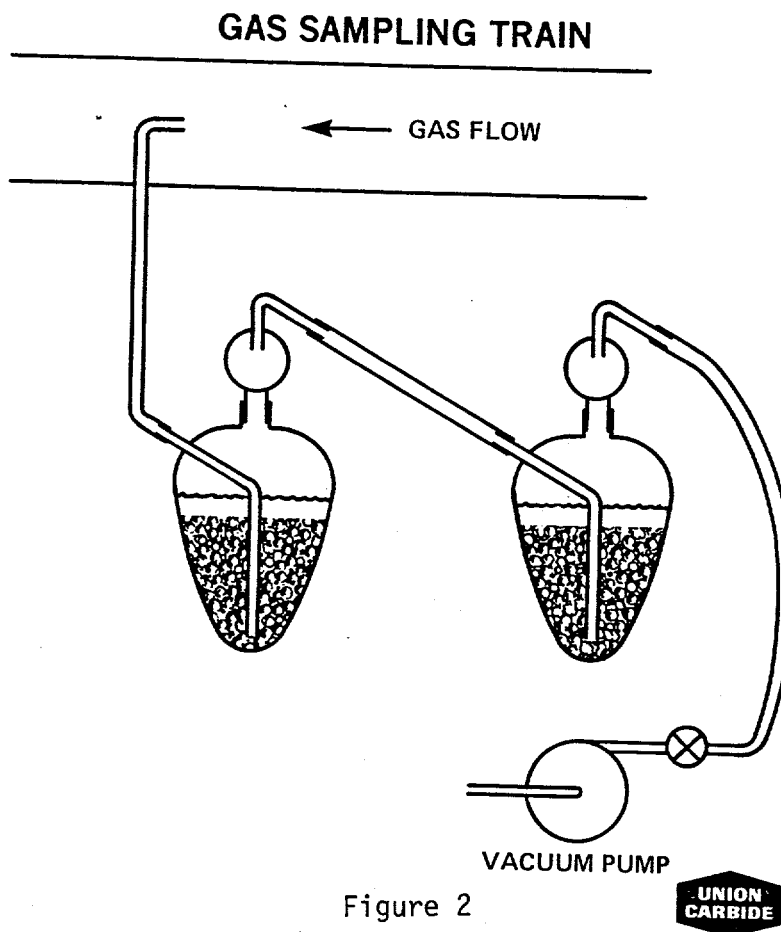


Figure 2

Depicted in Table 4 are methods of analysis and concentration ranges. Fluorides are determined by the SIE method. Chlorides are also determined by SIE.

Table 4

ANALYTICAL METHODS FOR GAS SAMPLES

Parameter	Method	Range, $\mu\text{g}/\text{ft}^3$	
		Inlet	Outlet
F	Selective Ion Electrode	70-40,000	0.2-5000
U	TOPO Extraction with Fluorimetry	0.1-1,000	0.1-500
Cl	Selective Ion Electrode	10-6,000	1-2000
Tc	Radiochemistry		0.001-0.01

Because of the low level of uranium present, uranium is determined fluorimetrically. Technetium is determined by radiochemistry using the beta liquid scintillation spectrometer.

Sampling of the outlet gas has been conducted at two locations since the program was initiated, and a third location is being considered. The initial sampling location was in close proximity to the outlet of the scrubber. As a result of problems encountered with liquid carry-over from the scrubber, the sampling location was moved to a location near the end of the exhaust line. Figure 3 shows the current sampling location.

EXHAUST GAS SAMPLING POINT

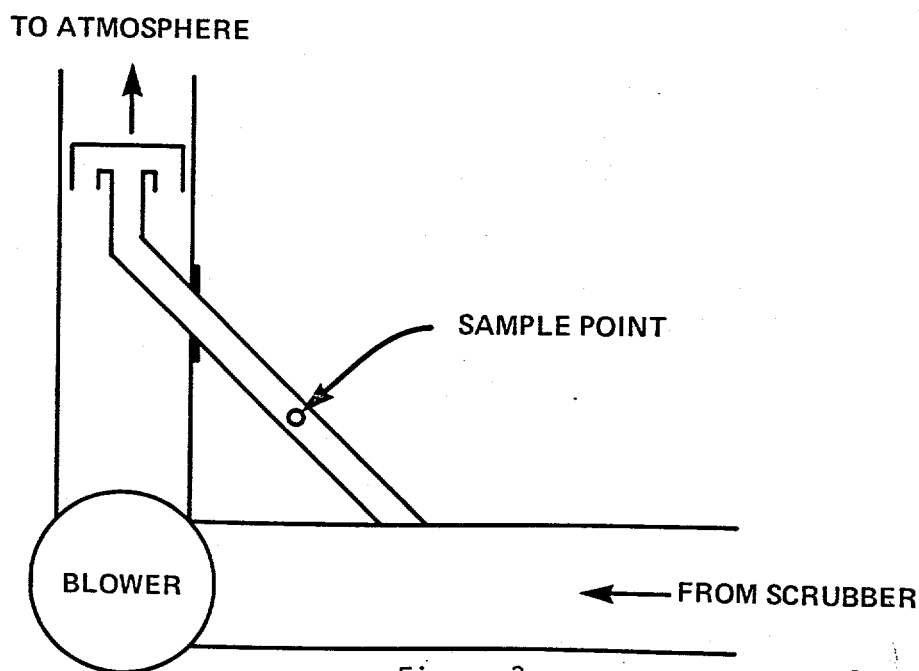


Figure 3



The vacuum from the exhaust blower is used to transfer a portion of the gas through the auxiliary sampling line from which a sample is taken. This system gives a sample from the exit end of the exhaust stack and minimizes the problem of liquid carry-over. Table 5 shows the effect of changing sampling location on measured levels of uranium, fluoride, and chloride.

Table 5
COMPARISON OF RESULTS FROM TWO
OUTLET SAMPLING LOCATIONS

Sampling Point 1 - close proximity to scrubber	
Sampling Point 2 - close proximity to stack outlet	
<u>Component</u>	<u>Average Ratio - $\frac{\text{Sampling Point 2}}{\text{Sampling Point 1}}$</u>
F	0.3
Cl	0.5
U	0.2

Recommendations have been made for still a third sampling system, which calls for the installation of a sampling probe in the area of the exit of the stack. This will minimize possible adverse effects caused by re-routing of the gas flow creating long sampling lines and extra restrictions to smooth flow in the sampling system. Also, since flow through the system varies with purge cascade operation, development of a system for automatically adjusting sampling flow is being considered.

In summary, we have presented a review of the analytical effort expended at ORGDP to support the operation of a purge cascade liquid scrubber. This report has dealt with the analysis of gases, solid and liquid by-products, and the scrubbing solution itself. Data derived from these samples are used to make decisions in the areas of process control, by-product disposal for safety, accountability, and environmental monitoring.

A similar report of this work (K/TL-770) was presented at the 22nd ORNL Conference on Analytical Chemistry in Energy Technology, October 11, 1978 in Gatlinburg, Tennessee.